Adhesion and Friction

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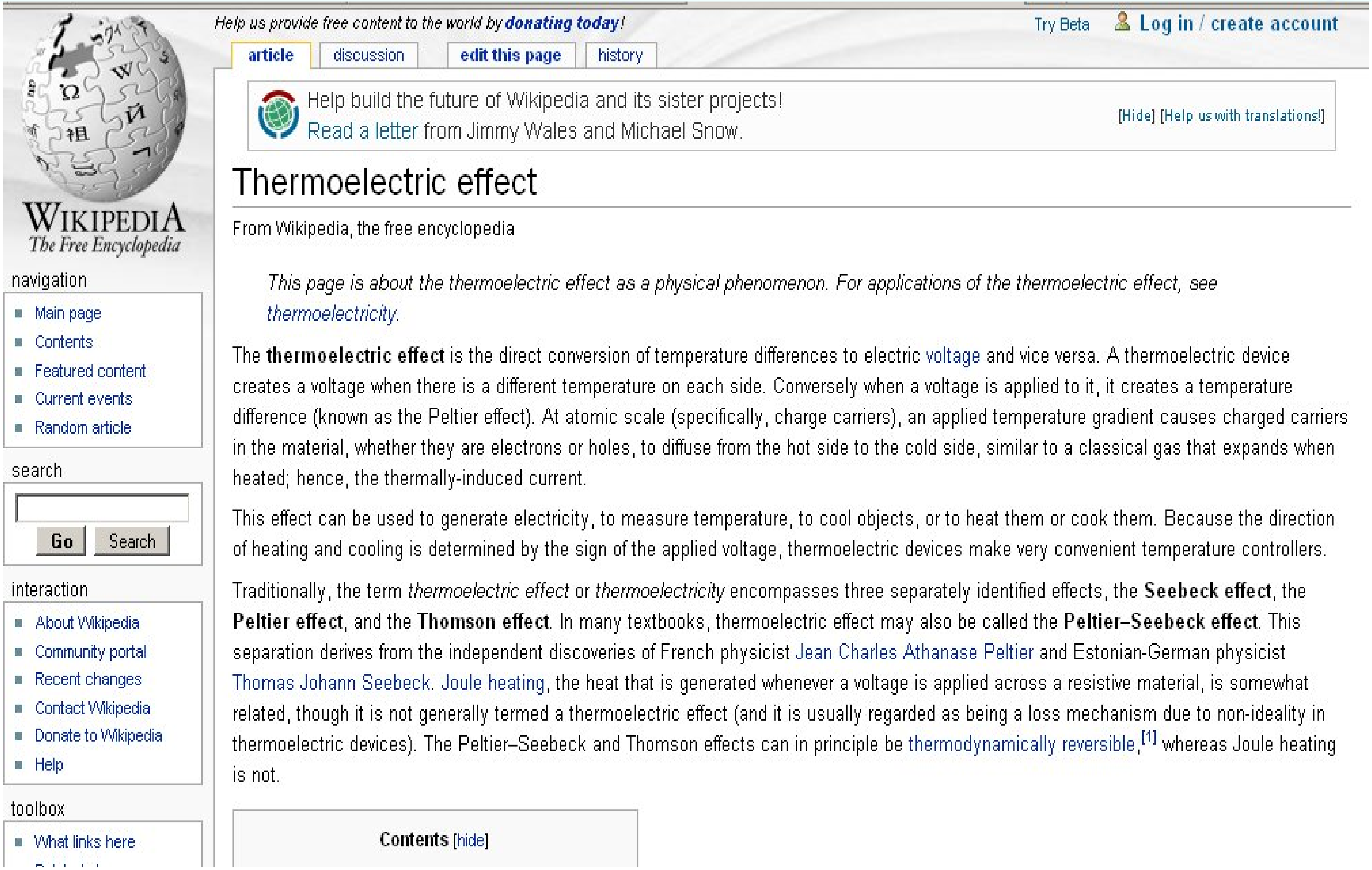
Course Website: **nanoHUB.org**
Compass.illinois.edu

About Final Project

- You are asked to create an entry of nanotechnology topic on Wikipedia

- Recommended Contents:
  - Background and History
  - Basic Principles
  - Size effect
  - Materials, Applications
  - Recent advancements
  - Links

Wikipedia Example



Help build the future of Wikipedia and its sister projects!
Read a letter from Jimmy Wales and Michael Snow.

Thermoelectric effect

From Wikipedia, the free encyclopedia

This page is about the thermoelectric effect as a physical phenomenon. For applications of the thermoelectric effect, see thermoelectricity.

The **thermoelectric effect** is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely when a voltage is applied to it, it creates a temperature difference (known as the Peltier effect). At atomic scale (specifically, charge carriers), an applied temperature gradient causes charged carriers in the material, whether they are electrons or holes, to diffuse from the hot side to the cold side, similar to a classical gas that expands when heated; hence, the thermally-induced current.

This effect can be used to generate electricity, to measure temperature, to cool objects, or to heat them or cook them. Because the direction of heating and cooling is determined by the sign of the applied voltage, thermoelectric devices make very convenient temperature controllers.

Traditionally, the term *thermoelectric effect* or *thermoelectricity* encompasses three separately identified effects, the **Seebeck effect**, the **Peltier effect**, and the **Thomson effect**. In many textbooks, thermoelectric effect may also be called the **Peltier–Seebeck effect**. This separation derives from the independent discoveries of French physicist Jean Charles Athanase Peltier and Estonian-German physicist Thomas Johann Seebeck. Joule heating, the heat that is generated whenever a voltage is applied across a resistive material, is somewhat related, though it is not generally termed a thermoelectric effect (and it is usually regarded as being a loss mechanism due to non-ideality in thermoelectric devices). The Peltier–Seebeck and Thomson effects can in principle be thermodynamically reversible,[1] whereas Joule heating is not.

Contents [hide]

Proposal Presentation

- Date: Oct 12-Oct 16
- Every one is given 15 minutes for your presentation:
  - What's your topic?
  - Why it is interesting?
  - What's the nanoscience principle?
  - Who are the heros in this area?
  - What would be the potential applications?

Organization of Coming Lectures

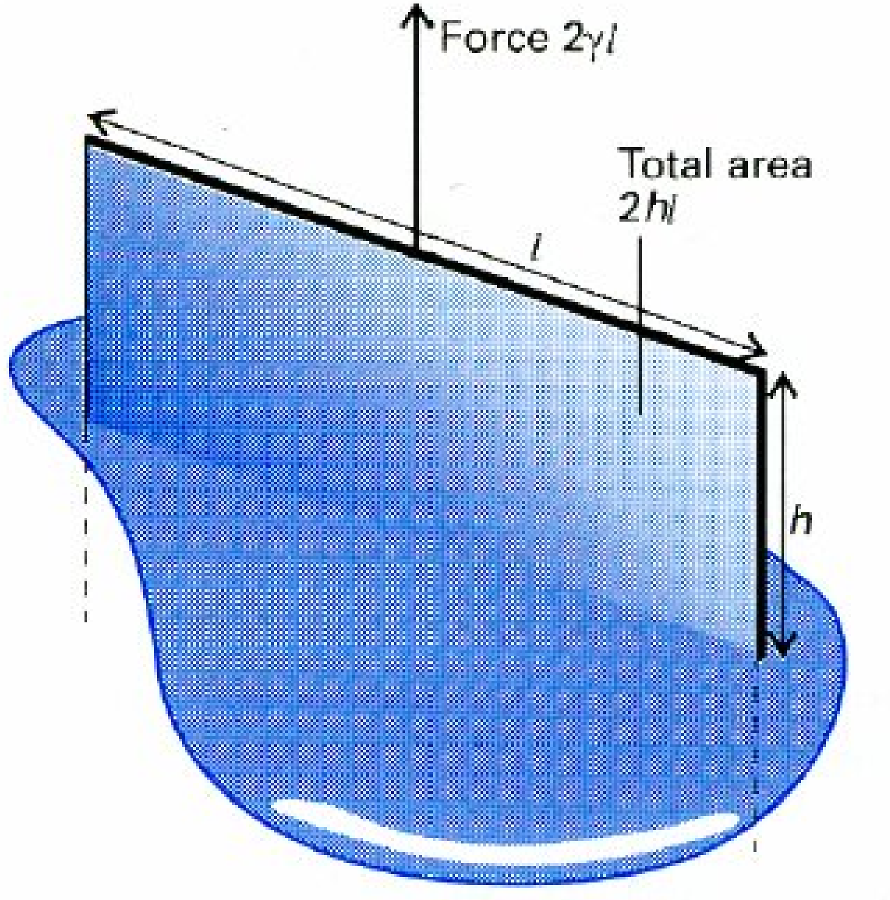
- Coupled Charge-Mass Transport in Fluid
  - Electrokinetic Phenomena
- **Surface and Interface Interactions**
  - Contact Angle, Effect on Melting and Condensation, Wetting on surface textures
- Adhesion and Friction

Surface and Surface Tension

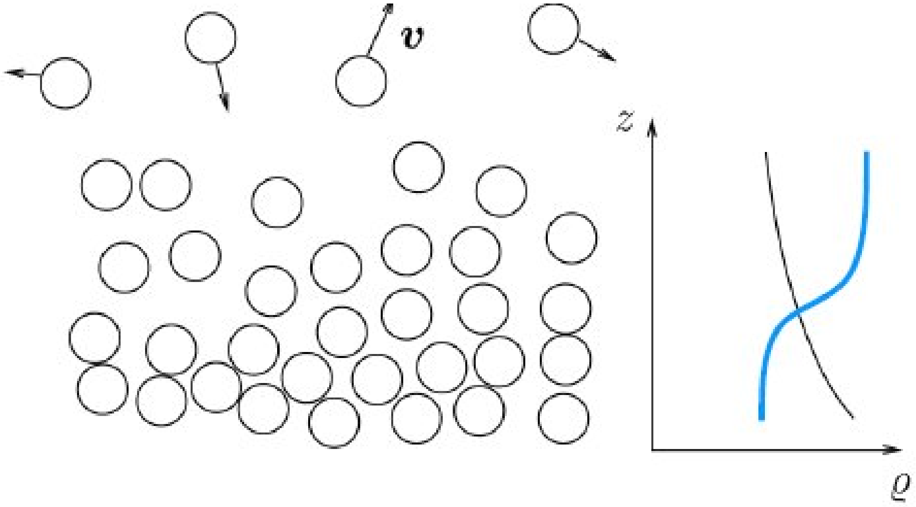
- Surface tension: a thermodynamic property

- $dG=\gamma dA$, $dF=\gamma dl$
- Unit : J/m^2 or N/m

Surface tension is generally restricted to liquid; Surface free energy generally applies to liquids and solids



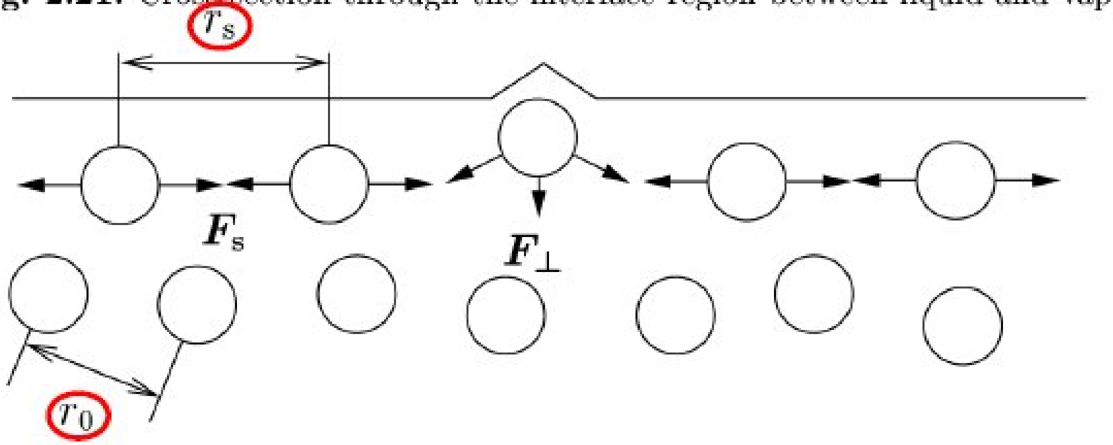
Molecular Picture of Surface Tension



Density distribution

Surface Potential

Fig. 2.21. Cross section through the interface region between liquid and vapor

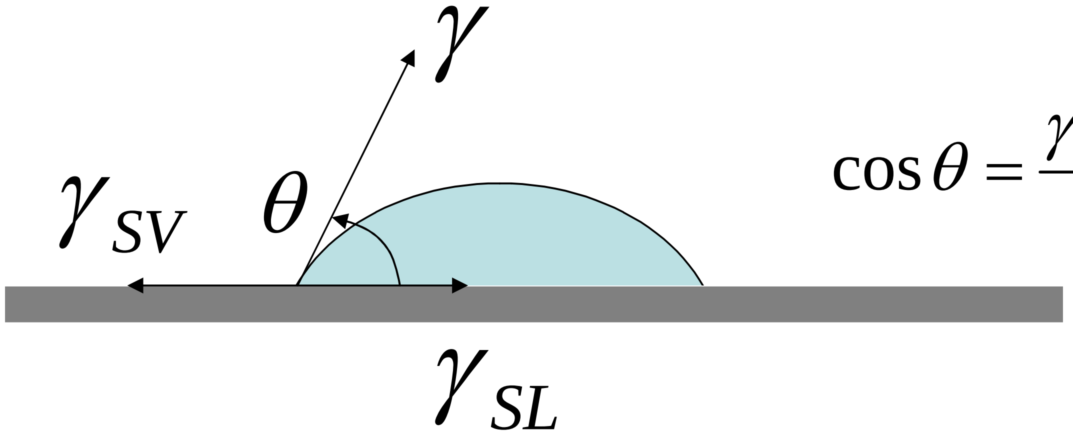


Surface forces

Fig. 2.22. Force $F_\perp$ on molecule moved perpendicular to surface plane results from perpendicular components $F_\perp$ of forces F_s acting in surface plane

From: Jens Ducrée, http://www.myfluidix.com/

Contact Angle: Young's Equation



$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma}$$

- Young's equation to relate the surface forces at the three-phase contact line to the apparent contact angle for an ideal surface.

$\theta =$ Young's angle for a smooth surface

where

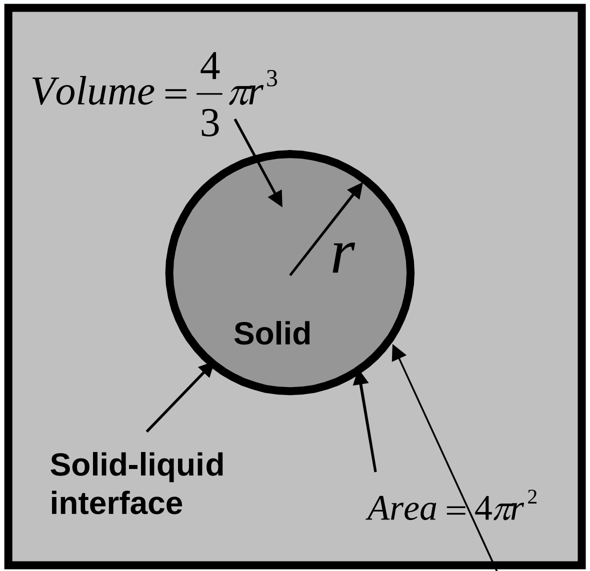
the interfacial energies

γ_{SV} : solid - vapor

γ_{SL} : solid - liquid

γ : liquid - vapor

Effect of Surface Energy: Nucleation/Melting



Volume (Bulk) Free Energy – stabilizes the nuclei (releases energy)

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

$$\Delta G_\upsilon = \frac{\text{volume free energy}}{\text{unit volume}}$$

Surface Free Energy- destabilizes the nuclei (it takes energy to make an interface)

$$\Delta G_S = 4\pi r^2 \gamma$$

γ = surface tension between solid-liquid interface

Solidification/Melting

$$r^* = \frac{-2\gamma T_m}{\Delta H_S \Delta T}$$

r^* = critical radius

γ = surface free energy

T_m = melting temperature

ΔH_S = latent heat of solidification

$\Delta T = T_m - T$ = supercooling

Note: ΔH_S = strong function of ΔT

γ = weak function of ΔT

$\therefore$ r^* decreases as ΔT increases

For typical ΔT r^* ca. 100Å

Bulk gold melts at 1,064°C.

3nm gold nanoparticles melts at 300°C!

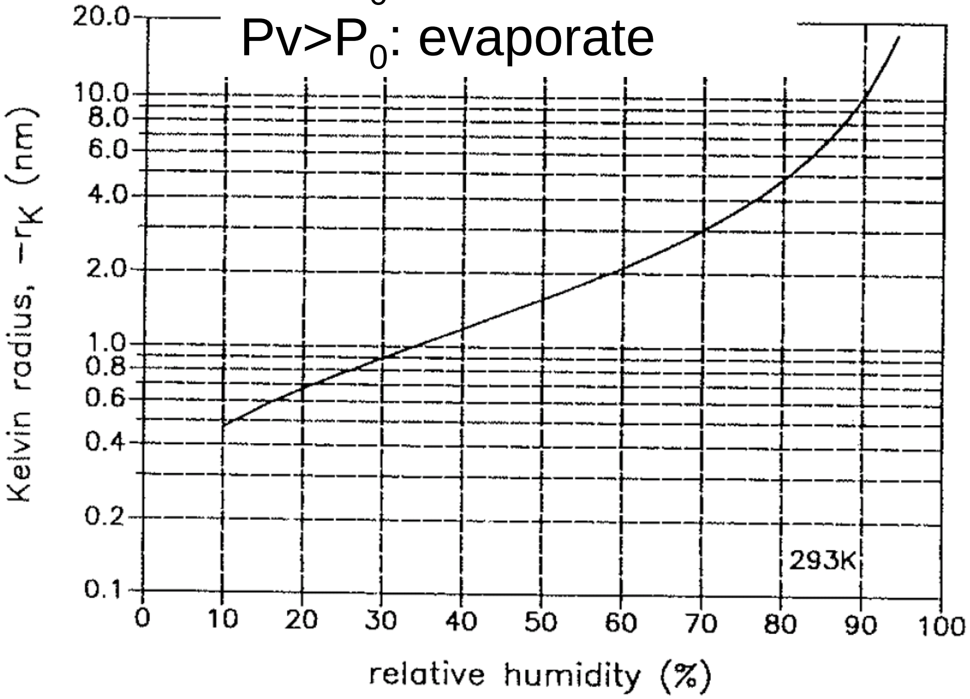
Size Effect in Evaporation/ Condensation

Kelvin Equation: The change in vapor pressure due to a meniscus with radius *r* (e.g. in a capillary or over a droplet)

$$\frac{2\gamma}{r} = nk_B T \ln\left(\frac{P_v}{P_0}\right)$$

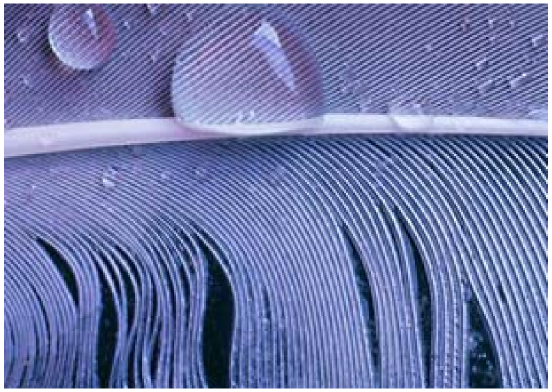
Pv<P_0: condense;
Pv>P_0: evaporate

- The surface tension of water is γ = 74mN/m at T = 293 K which gives the parameter γ/nkT = 0.54 nm.
- Therefore we obtain for a Kelvin radius of **100 nm (concave),** Pv/P_0 = 0.9.



Wetting on Textured Surfaces

- Nature has provided some water repelling examples from which we can learn.
  - Bird feathers
  - Lotus leaves
  - Water walking insects such as water striders and some types of spiders



http://chemistry.org/

http://www.treehugger.com/files/lotus-leaf.jpg

http://www-math.mit.edu/~dhu/Striderweb/striderweb.html

Wetting on Textures: Wenzel Model

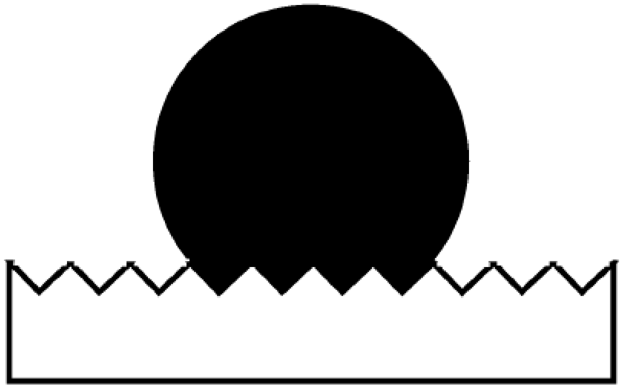
- Wenzel [2] showed that the apparent contact angle for homogeneous systems with surface roughness is modified in the following way:

$$\cos\theta_W = r\cos\theta$$

θ_W = Apparent contact angle for a Wenzel drop

$r \equiv \text{surface roughness} = \dfrac{\text{actual surface area}}{\text{geometric surface area}}$

θ = Young's angle for a smooth surface



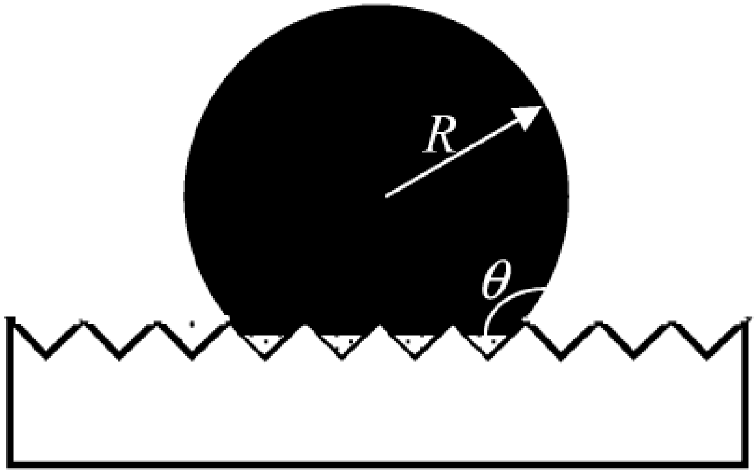
Marmur, *Wetting on hydrophobic rough surfaces: To be heterogeneous or not to be* [3]

Illustration of a drop in the Wenzel state on a rough surface; note homogeneous contact area

Inhomogeneous Wetting

- Cassie and Baxter [4] developed the following relation, sometimes referred to as Cassie's Law, to predict the apparent contact angle for heterogeneous systems based on wetted fractional areas

$$\cos\theta_C = \phi_s\left(r_w \cos\theta + 1\right) - 1$$



Marmur, *Wetting on hydrophobic rough surfaces: To be heterogeneous or not to be* [3]

θ_C = Apparent contact angle for a Cassie drop

ϕ_s = Wetted area fraction on the horizontal projected plane

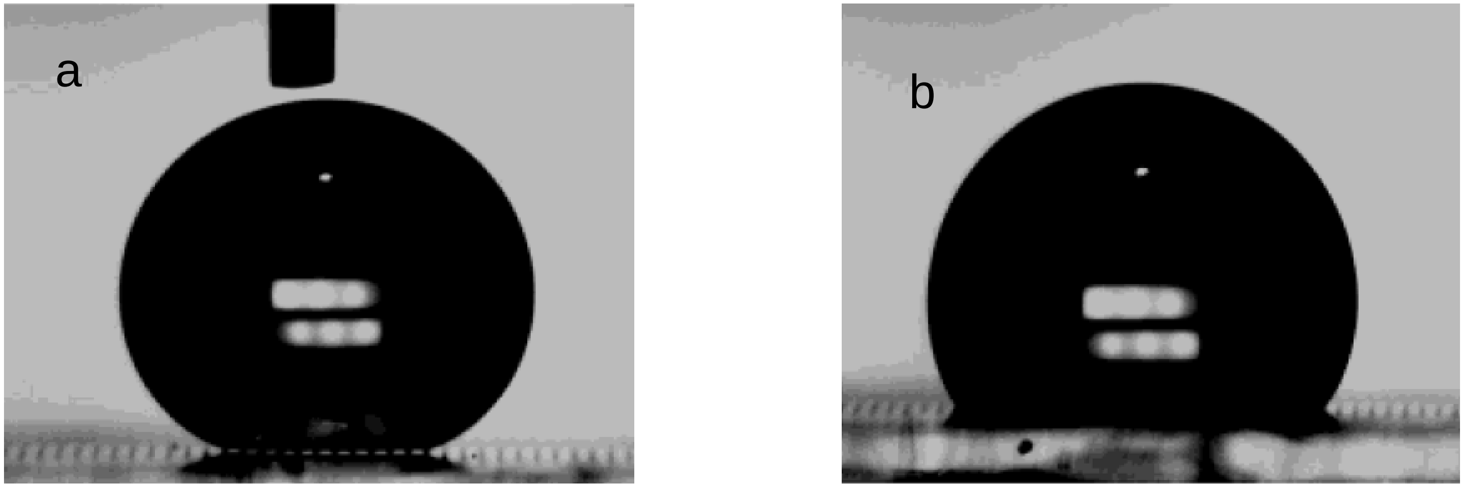
r_w = Surface roughness of the wetted area

θ = Young's angle for a smooth surface

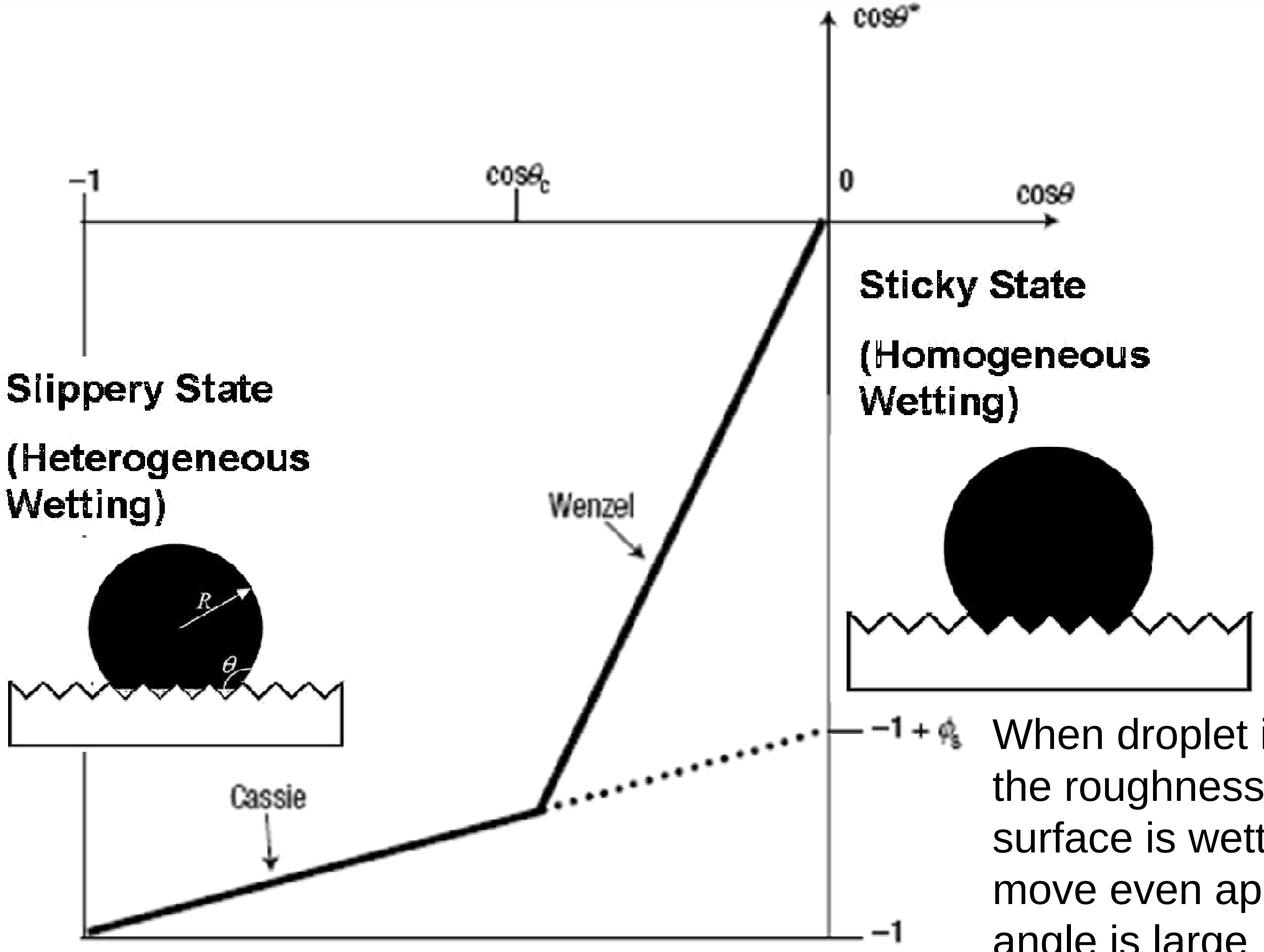
Illustration of a drop in the Cassie state on a rough surface; note heterogeneous contact area

Cassie and Wenzel States

- Here are a pair of excellent micrographs from Patankar showing actual droplets in the Cassie state (a) and the Wenzel state (b)
- Note, however, that they are sitting on exactly the same surface, indicating transitions are possible



Sticky or Slippery Surfaces?



Slippery State

(Heterogeneous Wetting)

Sticky State

(Homogeneous Wetting)

When droplet is comparable to the roughness and the original surface is wetting, it may not move even apparent contact angle is large

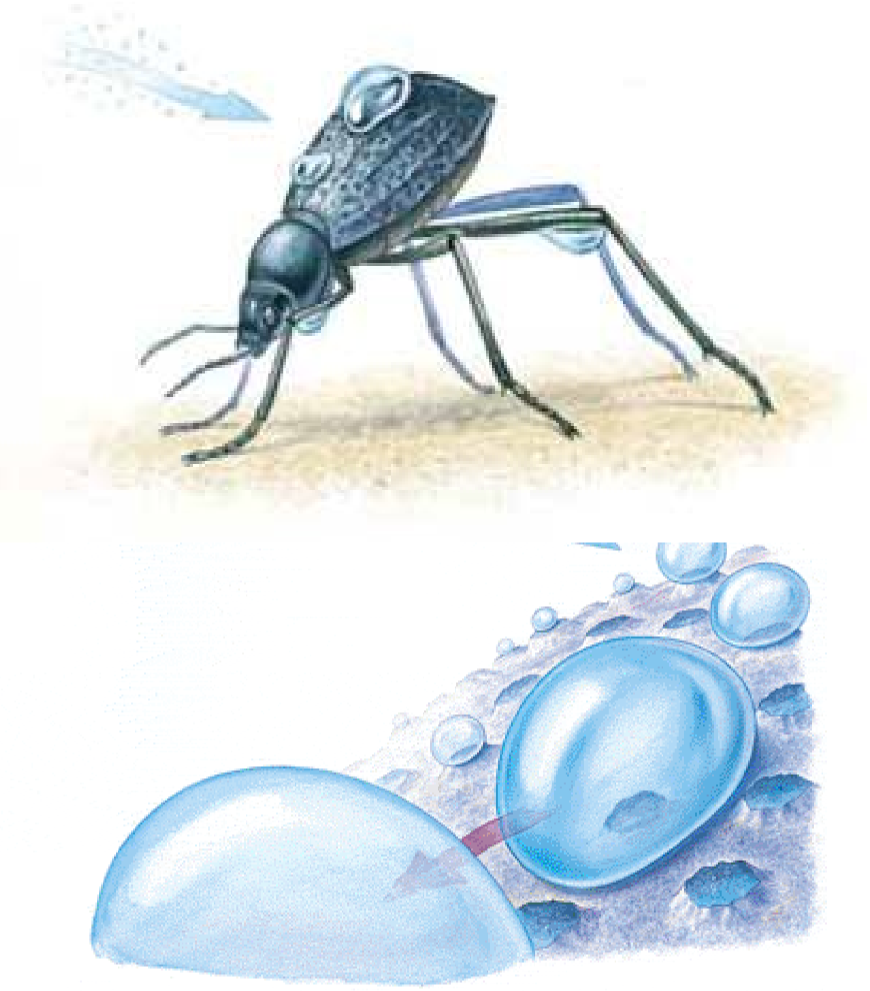
Nature’s Example: Namib Beetles

- **Imagine you’re a very thirsty tiny beetle in a desert. How can you get a drink?**

- ***Namib beetles have two types of surface bumps***

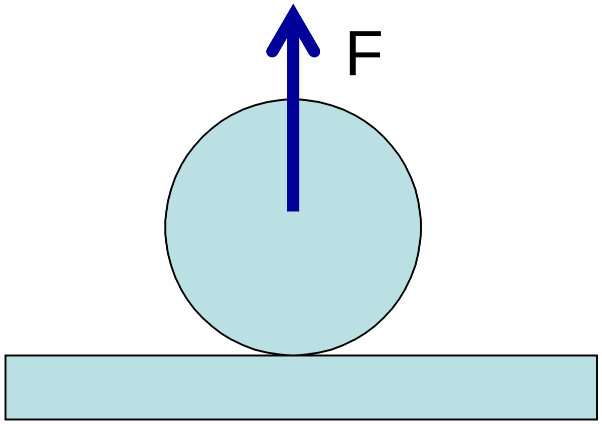
- unwaxed bumps to stick water droplets from the fog;

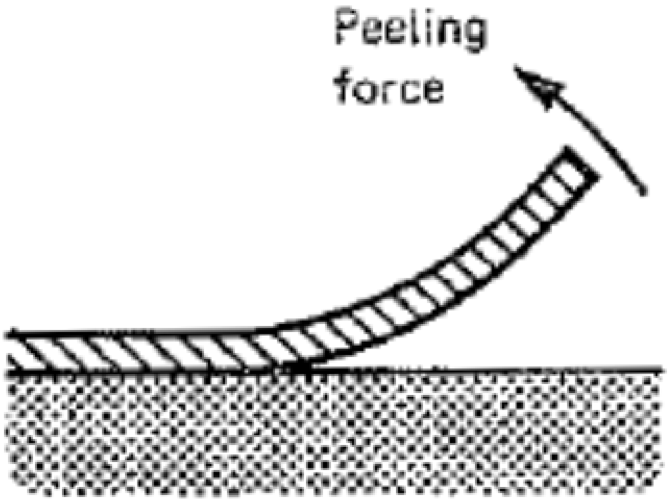
- waxed troughs with water-repellency, so the droplets roll into the mouth.



http://www.newscientist.com/article.ns?id=dn1508

Switching to Solid Surfaces





Surface interactions in practice:

- Pulling/Rolling a sphere on flat surface

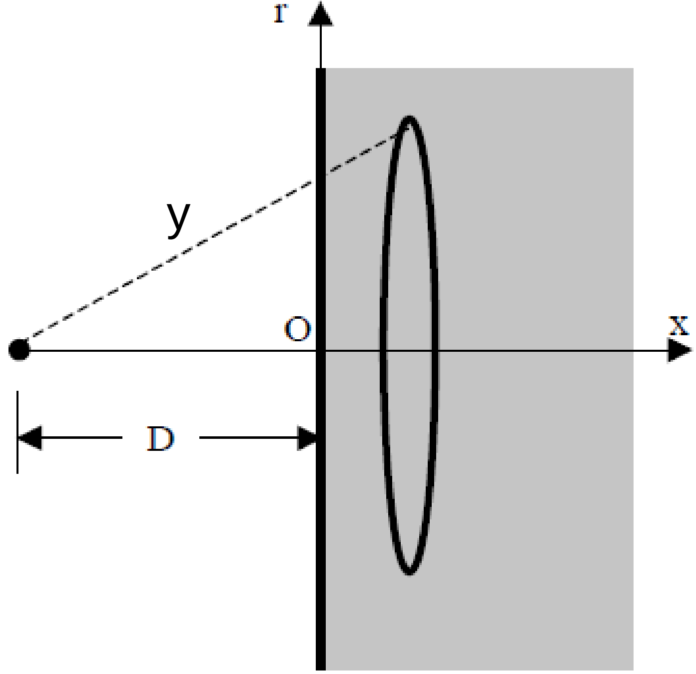
- Peeling test (tapes, adhesives)

So what determines the adhesion forces on these contacts in the molecular scale?

Origin of Adhesion: VdW Forces

- Van de Waals force: the long range interactions between molecules
- Recall the potential energy: $\phi = -\frac{\alpha}{r^6} \cancel{+ \frac{\beta}{r^n} \quad (n \approx 12)}$

Let's find the interaction between one molecule and a surface



At distance x in the wall, consider a circle of radius r:

$$y = \sqrt{(D + x)^2 + r^2}$$

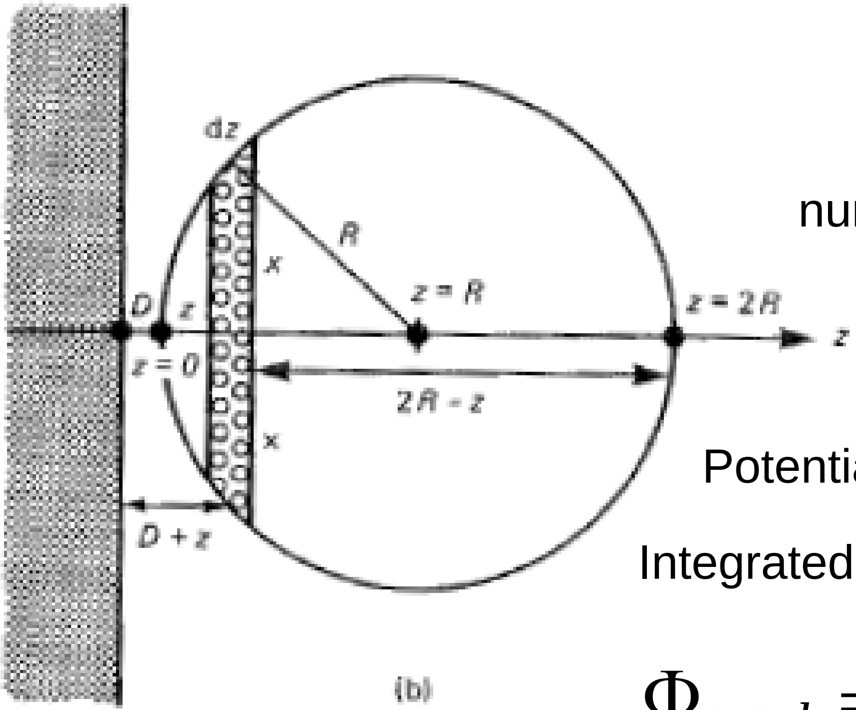
Number density of molecules in wall

$$\Phi(D) = \int_0^\infty \int_0^\infty \rho \phi(y) 2\pi r dr dx$$

$$\Phi(D) = -\frac{\pi\rho\alpha}{6D^3}$$

Example: Cylinder to Flat Surface

Consider a thin sheet at location *z* on the sphere:



From: Israelachvili 2nd Ed

Radius $x = \sqrt{(2R - z)z}$

number of molecules on this sheet:

$$\rho_2 \pi x^2 dz = \rho_2 \pi (2R - z) z dz$$

Potential energy per molecule: $\Phi(D+z) = -\frac{\pi \rho_1 \alpha}{6(D+z)^3}$

Integrated over whole sphere:

$$\Phi_{total} = -\rho_1 \rho_2 \pi^2 \alpha \int_0^{2R} \frac{(2R - z)z}{6(D+z)^3} dz$$

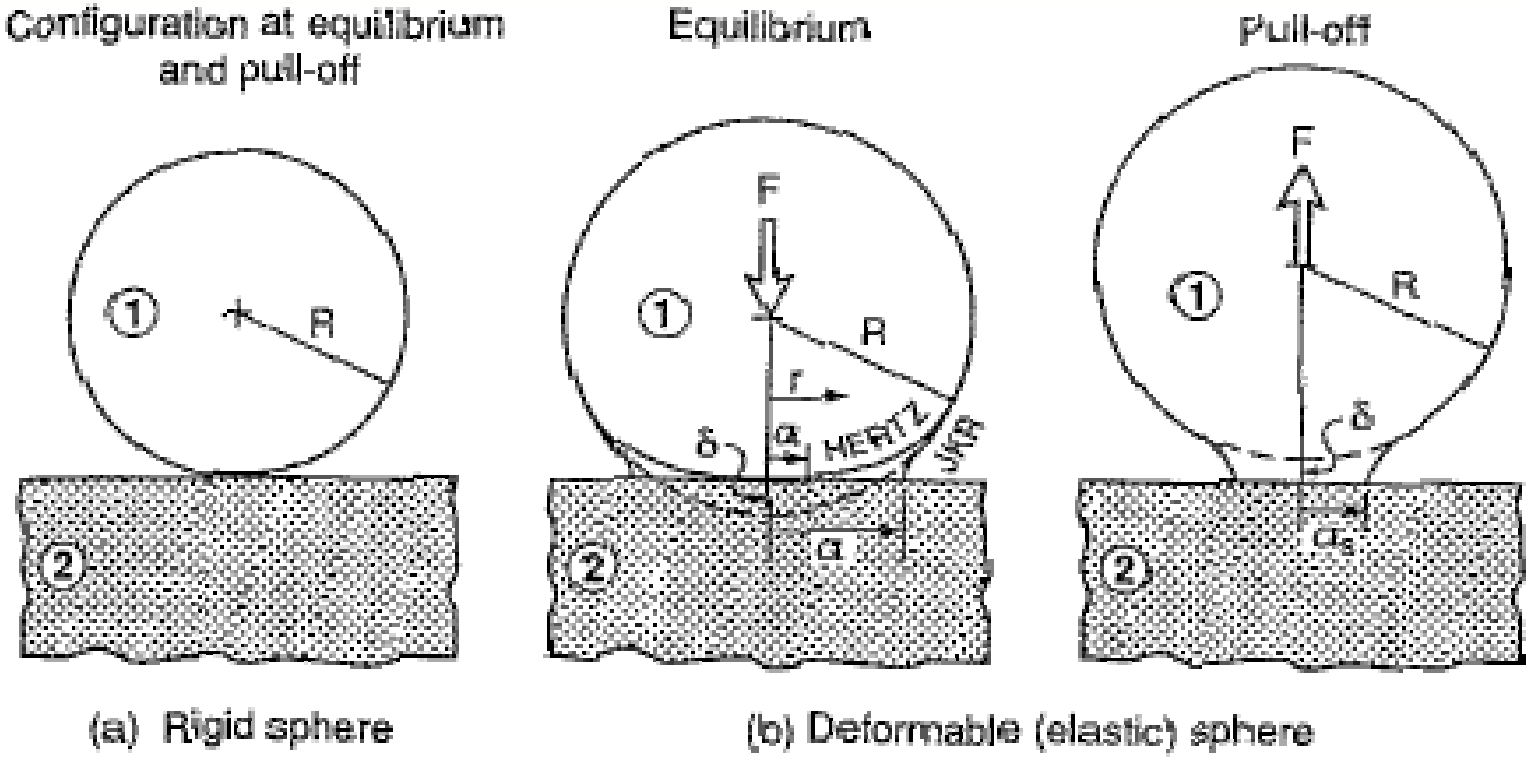
When D<<R, 2R-z ~2R

$$\Phi_{total}(D) \approx -\frac{\rho_1 \rho_2 \alpha \pi^2 R}{6D}$$

Size of contact

Distance of contact

Johnson-Kendal-Roberts Model



Configuration at equilibrium and pull-off

Equilibrium

Pull-off

(a) Rigid sphere

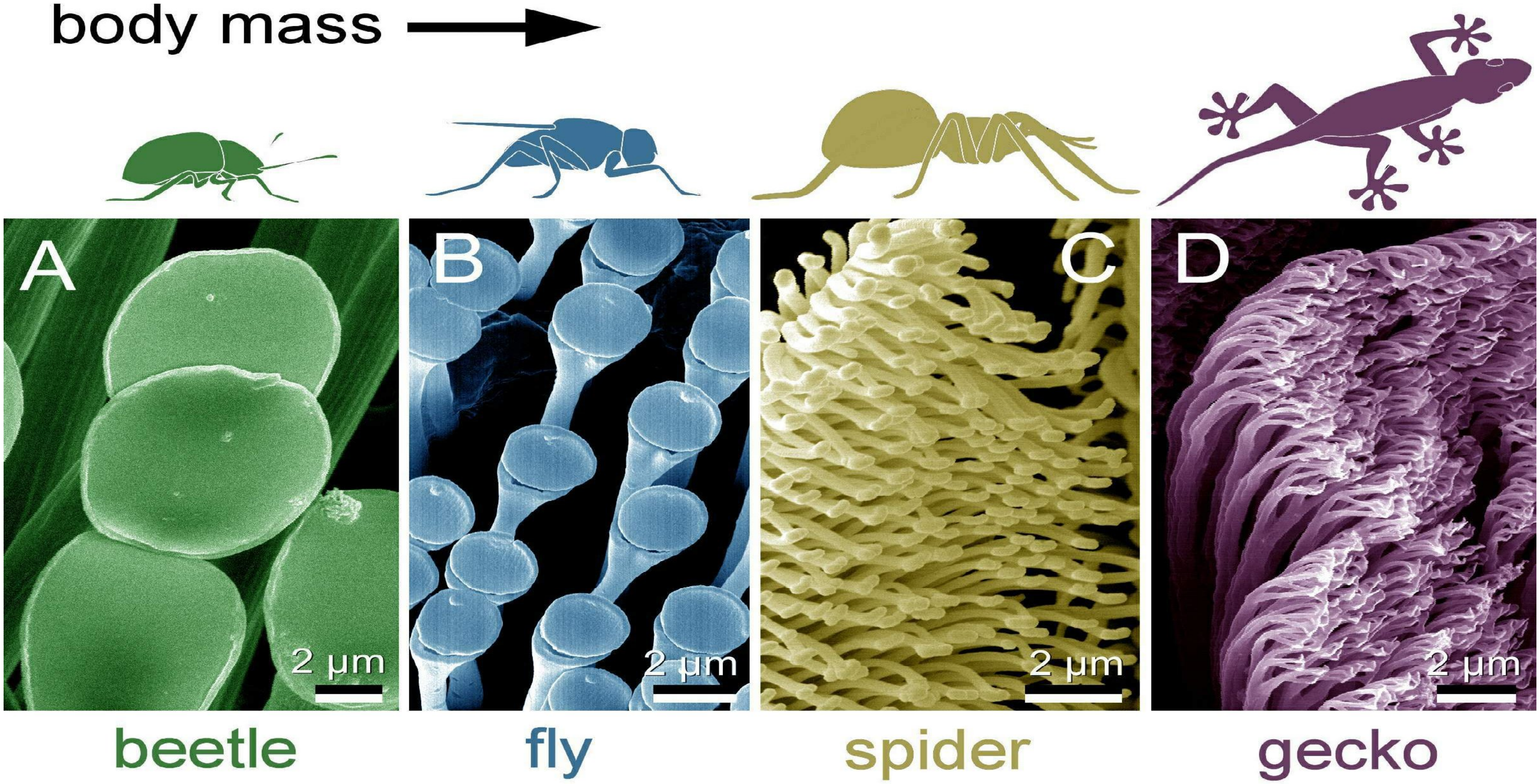
(b) Deformable (elastic) sphere

Fig. 15.7. (a) Rigid sphere on rigid surface. (b) Left: deformable (elastic) sphere on rigid surface in the absence (Hertz) and presence (JKR) of adhesion. Right: elastic adhering sphere about to separate spontaneously from adhesive contact.

From Israelachvili

Considering elasticity and surface energy, the JKR model leads to modern theory of contact mechanics

Adhesion Enhancement by Nano-toes



http://shasta.mpi-stuttgart.mpg.de/research/Bio-tribology.htm

$$\Phi(R,D) = -\frac{\rho_1 \rho_2 \pi^2 \alpha R}{6D}$$

As sticky as a Gecko?

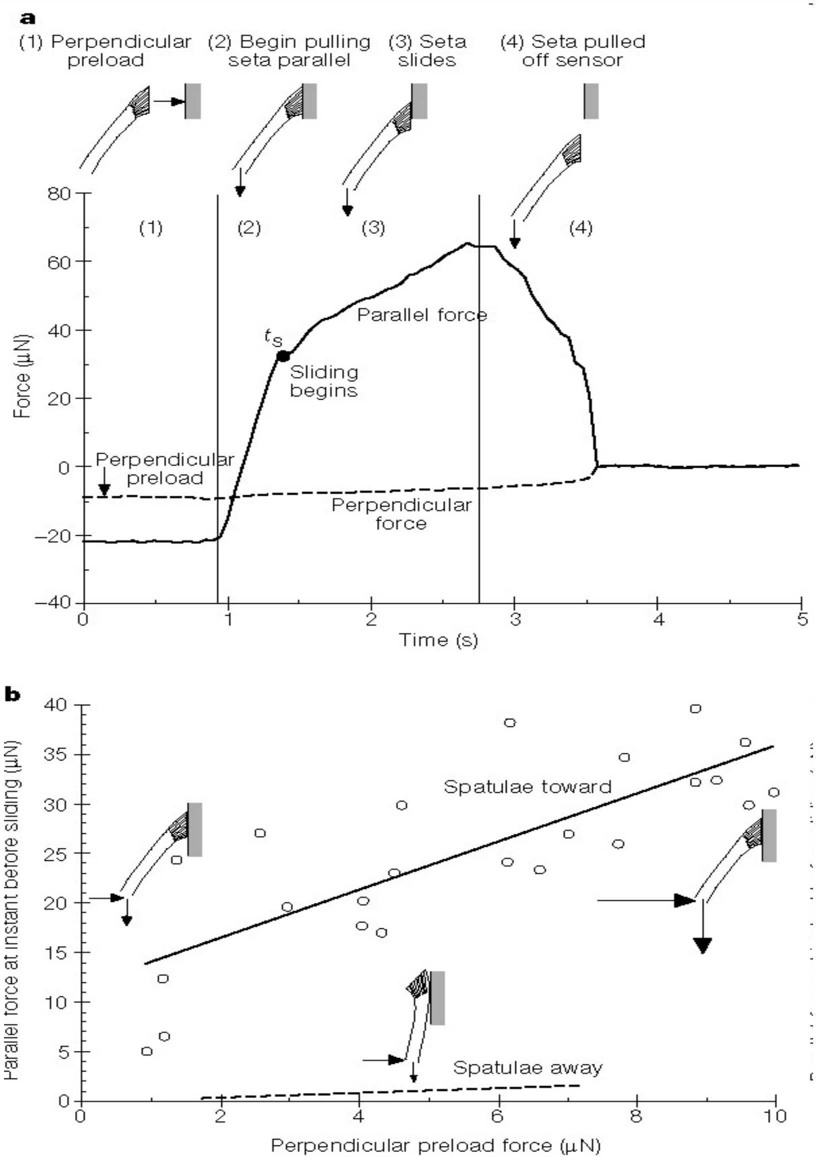
Autumn K et al. PNAS 2002;99:12252-12256

Tokay Gecko Stats:

- 500,000 hairs per toe
- Hundreds of nanoprojections (spatulae) per hair
- Adhesive force in one foot = 100 newtons
- One dime-sized spot could lift a child weighing 45 pounds.

Question Arising: ***If their feet are <u>that</u> sticky, how do they pick up their feet?***

How Can a Gecko Lift Its Foot Off?



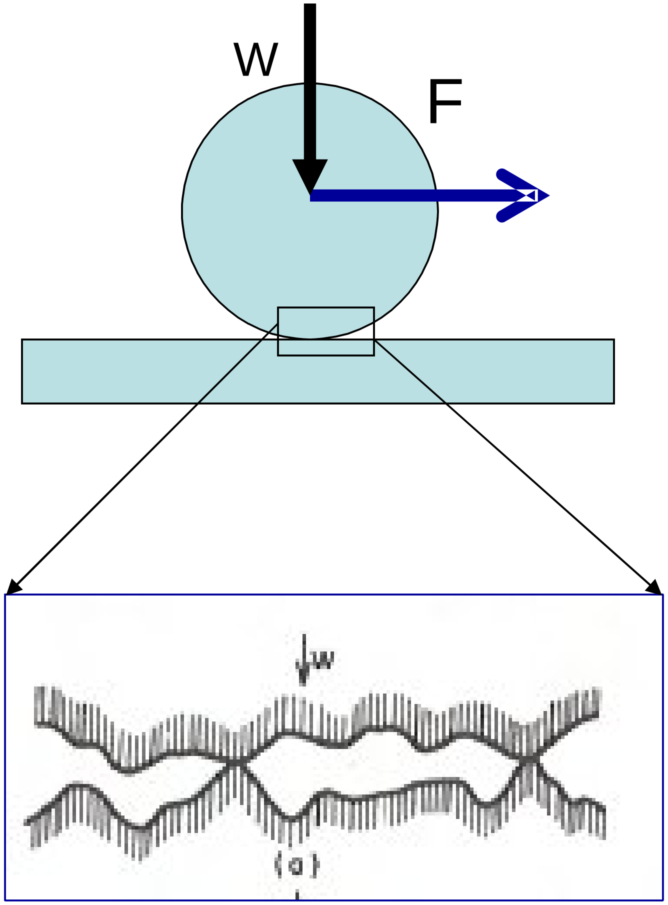
"These lizards uncurl their toes like a paper party favor whistle when putting their feet down;

- and peel the toes back up as if removing a piece of tape when they step away."

Chemical & Engineering News, 2000

K. Autumn et al, Nature 405, 681-685(2000)

Microscopic View of Friction



$$F \approx \frac{A}{D}(\underline{\gamma_A} - \underline{\gamma_R})$$

Surface energy in Advancing contact

Surface energy in Receding contact

Derjaguin (1957) proposed correction of friction

$$F \approx \mu W + \underline{\mu A p_0}$$

Due to adhesion energy (no external force needed)

Additional Readings

- Jacob N. Israelachvili, ***Intermolecular and Surface Forces***, Chapt 10,11,15, Academic Press, 2nd Edition, 1992 (available online)
- Adamson and Gast, “*Physical Chemistry of Surfaces*”, Chapt 12 , Wiley, 6th Edition.